The Spatial Structure of Tetrabenzoheptafulvalene[1]

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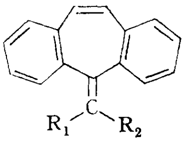
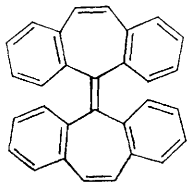
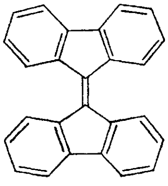
THE question whether the dibenzoheptafulvenes (I) are planar or not has been discussed on various occasions, but no final answer has yet been put forward.[2,3] This is particularly true for the case of the tetrabenzoheptafulvalene (II).[4—6] Amongst the methods which might lead to a *decision*, we have studied the n.m.r. spectrum of (II). This spectrum† is composed of four multiplets and one singlet as follows: (*a*) quartet: 6·535, 6·550, 6·610, and 6·625 p.p.m.; J_1 1·5, J_2 6·0, J_3 1·5 c./sec. (*b*) sextet: 6·800, 6·815, 6·875, 6·890, 6·947, and 6·960 p.p.m.; J_1 1·5, J_2 6·0, J_3 1·3, J_4 5·9, J_5 1·3 c./sec. (*c*) sextet: 6·975, 6·990, 7·050, 7·063, 7·122, and 7·135 p.p.m.; J_1 1·5, J_2 6·0, J_3 1·3, J_4 5·9, J_5 1·3 c./sec. (*d*) singlet: 7·085 p.p.m. (*e*) triplet: 7·253, 7·310, and 7·326 p.p.m.; J_2 5·7, J_3 1·6 c./sec. (this multiplet is in reality a quartet, the fourth peak at 7·238—7·240 p.p.m. being hidden by the absorption due to $CHCl_3$). The quartets (*a*) and (*e*) of type AB represent four hydrogen atoms which have only one neighbour in the *ortho*-position, H-1, -4, -5, -8 (and H-1′, -4′, -5′, -8′). The sextets (*b*) and (*c*) of type AB_2 correspond to four hydrogen atoms which possess two *ortho*-hydrogen atoms each, H-2, -3, -6, -7 (and H-2′, -3′, -6′, -7′). The singlet (*d*) represents the two other (equivalent) hydrogen atoms, H-9, -10 (and H-9′, 10′).[7]



(I)



(II)



(III)

The quartet at higher field [quartet (*a*), centre at 6·58 p.p.m.] shows unequivocally that the molecule (II) is not planar. Since it cannot represent H-4 and H-5 (and H-4′ and -5′), it must be assigned to the four hydrogen atoms *ortho* to the central double bond, *i.e.*, H-1, -8, -1′, -8′. Consequently, quartet (*e*) represents H-4, -5, -4′, -5′. For similar reasons, sextet (*b*) should be assigned to H-2, -7, -2′, -7′, and sextet (*d*) to H-3, -6, -3′, -6′. (In this case the

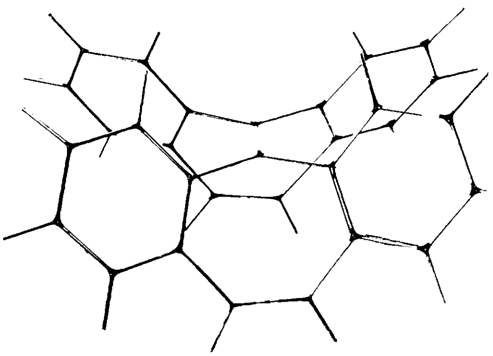


FIGURE 1. *Tetrabenzoheptofulvalene, model of* cisoid conformation.

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† Taken in $CDCl_3$ with a Varian HA 100 spectrometer.

shielding effect is much less pronounced, as expected). *A priori*, a nonplanar molecule of (II) can exist in two conformations: a *cisoid* (Figure 1) and a *transoid* (Figure 2). These conformations should differ in the absorption of the four hydrogen atoms *ortho* to the central double bond: *cisoid* conformation requires a strong interaction between H-1 and H-8′ (and between H-8 and H-1′), leading to an absorption at *lower* field than normal aromatic hydrogen atoms. Such an interaction was observed in the case of the analogous tetrabenzopentafulvalene (III).[8] On the other hand, in the *transoid* conformation each hydrogen atom *ortho* to the central double bond lies above (or below) the plane of the other half of the molecule, leading to an absorption at *higher* field than normal aromatic hydrogen atoms. Thus, the n.m.r. spectrum of (II) and particularly the shielding of 0·65 p.p.m. of quartet (*a*) proves not only that the molecule (II) is not planar, but in addition that it has the *transoid* conformation. It is worthy of note that an analogous structure has been found for the non-annellated heptafulvalene by *X*-ray diffraction of its crystalline form.[9]

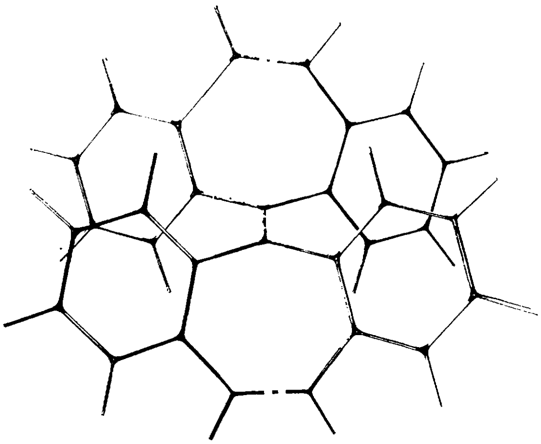

FIGURE 2. *Tetrabenzoheptafulvalene, model of* transoid *comformation.*

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